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Properties of new NIR-materials – gallium arsenide-phosphide solid solutions alloyed by bismuth

FUNCTIONAL ELECTRICAL AND ELECTRONIC MATERIALS AND DEVICES

Introduction

In optoelectronics the increasing attention is involved with multicomponent solid solutions A3B5 with band gap $E_g \geq 1,6$ eV as they are suitable for radiation of seen light. Use in heterosystems of the isovalent components actively influencing band structure of solid solutions (such as nitrogen and bismuth) opens ample opportunities in management of a luminescence spectrum, that allows to create the pairs connected on radiation – light emitting diodes (LEDs)–photodetectors. However in technology of such solid solutions there are substantial difficulties dealt with the limited solubility of bismuth in solutions-melts A3B5. Solubility of bismuth in GaP is more than on the order less than of nitrogen [1]. Besides according to the data of the last years [2] bismuth doping of solid solutions A3B5 gives a number of advantages, in particular, improvement of morphological stability of crystallization front, reduction of A3B5 structure deviation from stoichiometry, a possibility to change distribution coefficients of background and doping elements because of the interaction with doping elements in solutions-melts.

The problem of solubility can be solved by development of the appropriate technology.

Samples and the experiments technique

Calculation of quasichemical equilibria of liquid and solid phases was carried out in view of arrangement effects in a solid solution and influences of elastic strains. In the basic experiments with substrates plates gallium phosphide (111) were used, 25 mm in diameter and 200 microns in thickness alloyed with ZnO up to $n \sim 2,5 \times 10^{17}$ sm^{-3}. As a source plates GaAs were used. Packed “sandwiches” were loaded into the technological cartridge (fig. 1). Recrystallizing was operated in the hydrogen atmosphere by a temperature gradient field zone recrystallization technique “Raduga” consisting of a

hermetic reactor, purification system for hydrogen and resistive heaters with electronic system of stabilization and control temperature mode computer system. Zones velocity made 0.05–0.15 mcm/min at temperatures 950–980°C and grew at increase of the bismuth contents in a melt. Control of a temperature-time mode was programmed at IBM with supplementary analog-to-digital and digital-to-analog converters.

In the first series of experiments epitaxial layers GaP<Bi>/GaP were grown. The compositions close to received in [3] were programmed. The received layers had high concentration of carriers (~ 10^{18} sm^{-3}). In the subsequent series films $GaAs_xP_{1-x}$<Bi> were brought up, they were homogeneous on structure (0.1<x<0.5, y<0.35) with thickness up to 2 microns.

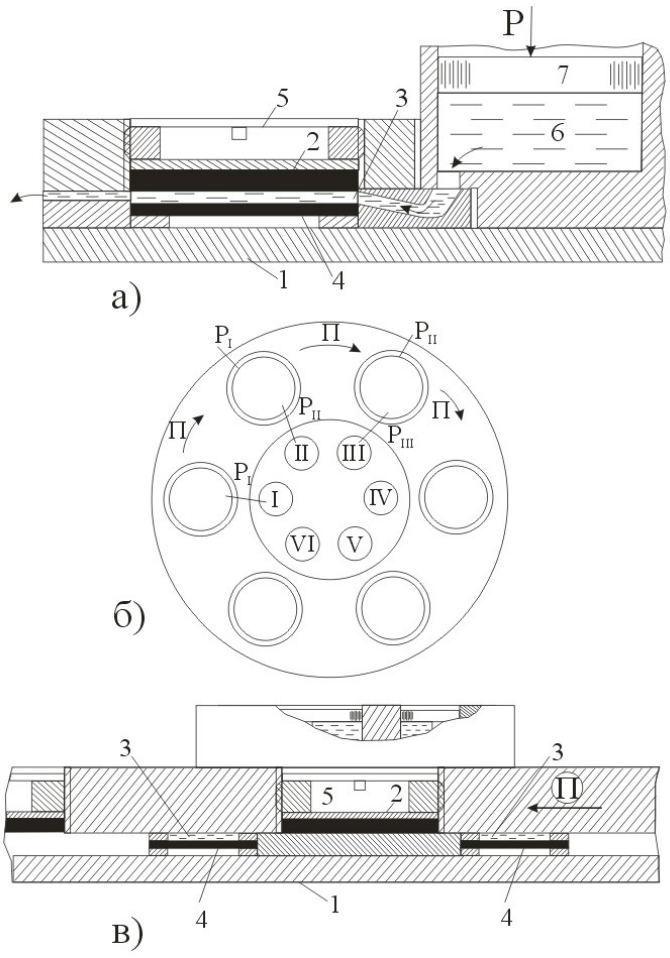

Fig. 1. The scheme of graphite technological cartridges: а) – a piston and б) – a shift types, в) – a containers rotation system.
P_I, P_{II}, P_{III}, etc. – packed "sandwiches" and the containers determined to them with certain solutions-melts squeezed out by a piston, П – rotation

Table 1.
Electrophysical characteristics for heterostructures $GaAs_xP_{1-x}$<Bi>/GaP

x	X^S_{Bi}	$n \cdot 10^{-18}$ sm^{-3}	μ, sm^2 / (V·s)
0.12	-	5.7	175
0.17	-	5.4	160
0.25	-	9.8	185
0.35	0.0004	14.8	230
0.30	0.0006	17.5	245
0.45	0.0010	18.9	260

Experimental results and their discussion

Solid phase structure was measured on the X-rays microanalyzer CAMEBAX with use of lines As-Lα, P-Lα, In-Lα, Ga-Lα and Bi-Mα. Experimental electrophysical characteristics of $GaAs_xP_{1-x}$<Bi>/GaP heterostructures are resulted in table 1 in comparison with $GaAs_xP_{1-x}$ solid solutions characteristics (without bismuth doping).

One can see that carrier concentration (n) and mobility (μ) appreciably grow with bismuth content increasing in a solid phase X^S_{Bi}. However the opportunity of the carriers concentration control with a variation of the bismuth content is limited to behaviour ambiguity of Bi atoms. Bismuth is a semimetall with the big covalent atom radius (1,5 nm). The basic mechanism of bismuth atoms entry in the working layers of a heterostructure is introduction between units of a crystal lattice, that accompanies with effect of dimensional quantization [4]; with smaller probability Bi atoms can form radiating complexes in lattices with partial replacement of gallium atoms. For the analysis of interaction processes we used model of defects evolution described in [5] that was modified for one-electronic (isovalent) impurity.

At redistribution of atoms in a crystal lattice of system Ga-As-P-Bi the following reactions are possible:

$$Bi_L + V_{P(As)} \leftrightarrow Bi_{P(As)} \text{ (1)}; \quad Bi_L + P_P\ (As_{As}) \leftrightarrow Bi_{P(As)} + P_{i(\text{Asi})} \text{ (2)};$$

$$Bi_L + Ga_{Ga} \leftrightarrow BiGa + Gai \text{ (3)}; \quad Bi_L \leftrightarrow Bi_i \text{ (4)}.$$

Here symbol V_k – a vacancy in sublattice of the *k*-component, index *L* designates a liquid phase, *i* – area between lattice units.

Introduction of Bi atoms between units (4) results in a bend of a lattice aside a recrystallized layer. Growth of number of antistructural defects Bi_{Ga}, Bi_{In} causes ordering the arrangement of defects bending a lattice in the return side (Ga_i). The minimum of energy in such processes corresponds to alternation of both types defects-strains. Thus

formation in a crystal of a certain elastic superlattice from the local areas stretched by defects of introduction and compressed by strains is possible. The X-ray analysis of GaAsP<Bi> films structural data received in a temperature gradient field has shown, that at the bismuth content in solid phase X^S_{Bi}=0.0009 the formed structure is almost close to ideal. Photoresponses with relative intensity are no lower than 0.5 were received in a range 1,51–2,75 eV (GaAsP<Bi>) and 0,12–0,18 eV (InGaSb<Bi>), that is much wider than areas of a luminescence of appropriate multicomponent solid solutions not alloyed by bismuth.

Obviously, mutual compensation of the deformed areas is the factor determining properties of LEDs made from such structures. It is necessary to note, that the offered model of bismuth behavior is enough simplified and the calculation data received on its basis will be coordinated with experimental with a margin error 10–15 %. Specification of the model demands the precision measurements spent directly during the films growth.

In [5] it is shown, that at optimum concentration of an impurity with the big atom volume the external quantum LEDs output β_{ex} achieves a maximum and LEDs have the least speed of this parameter degradation.

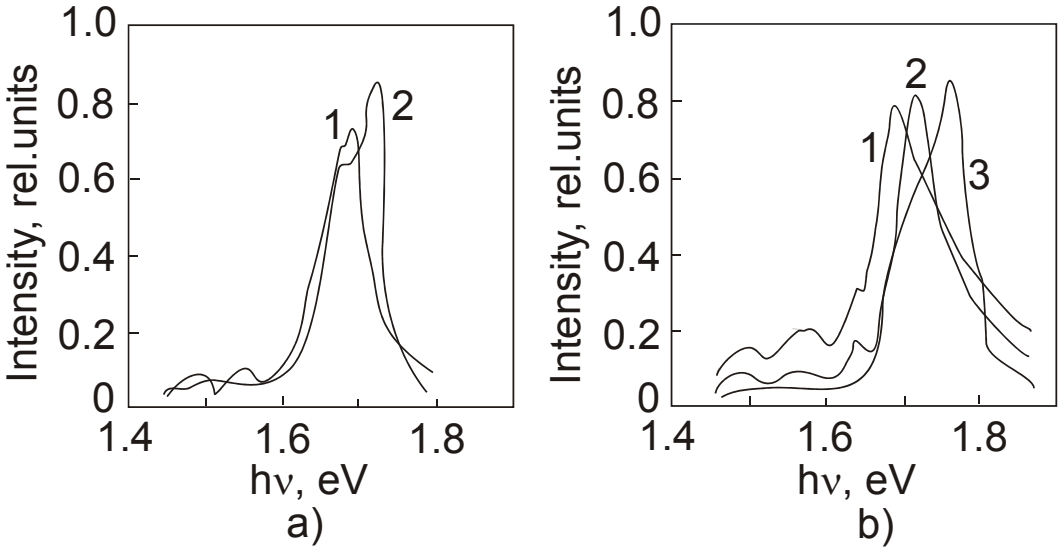

Fig. 2. Heterostructures GaP<Bi>/GaP (a) and GaAsP<Bi>/GaP (b) spectra of a luminescence. Bismuth content in the solid phase X^S_{Bi}, mol.%: 1 – 0,03; 2 – 0,06; 3 – 0,1.

Luminescent characteristics of heterostructures GaP<Bi>/GaP and GaAsP<Bi>/GaP were defined at 77 and 300 K. Spectra of a luminescence had at 77 K some maxima (fig. 2). Intensity of high-energy peaks did not vary at small changes of the gallium

arsenide content in GaAsPBi/GaP heterostructures. Semiwidth of peaks made 10–30 meV. The low-energy peaks caused by forming of complexes P and GaAs had relative intensity no more than 0,3. On fig. 2 it is visible that with growth of X^S_{Bi} intensity of low-energy peaks decreases and it's observed almost their disappearance that specifies on an arrangement role of bismuth.

The fact of additional displacement of a luminescence in short-wave area of a spectrum is found out at maximal values X^S_{Bi}. Probably, it is caused by increase of band gap E_g owing to Bernstein effect.

The maximum of regional radiation of a luminescence (300 K) corresponded to a maximum of calculation curve of E_g dependence from composition of a solid solution.

Conclusions

In a temperature gradient field epitaxial films of emitting heterostructures GaP<Bi>/GaP and GaAsP<Bi>/GaP are received. The model of the entry mechanism of bismuth as one-electronic impurity in a crystal lattice of solid solutions A3B5 (on the basis of which the observably phenomena are qualitatively described) is developed. Luminescent properties of bismuth doped films crystallized in systems Ga-P, Ga-As-P are investigated. The possibility of creation on their basis of injection emitters is shown.

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